

PROCEEDINGS OF

**THE 20<sup>th</sup> INTERNATIONAL SYMPOSIUM ON  
ANALYTICAL AND ENVIRONMENTAL PROBLEMS**

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**THE 20<sup>th</sup> INTERNATIONAL SYMPOSIUM ON ANALYTICAL AND  
ENVIRONMENTAL PROBLEMS**

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## THE EFFECT OF RADICAL TRANSFER MATERIALS ( $O_2$ , $HCOOH$ , $HCOONa$ ) ON VACUUM ULTRAVIOLET PHOTOLYSIS OF IBUPROFEN

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### ABSTRACT

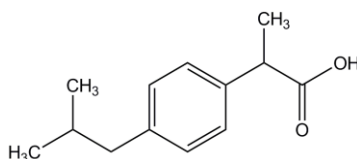
Nowadays, one of the emerging additive technologies for treatment of water are advanced oxidation processes (AOPs), which are based on the generation of reactive free radicals to induce the transformation of the organic contaminants. Vacuum ultraviolet (VUV) photolysis is a clear and easy method for the generation of reactive radicals (hydroxyl ( $\cdot OH$ ) and hydrogen ( $H\cdot$ ) radicals) without the addition of chemicals, using Xe excimer lamp ( $\lambda_{max}=172$  nm).

During this work the VUV photolytic degradation of ibuprofen (a non-steroidal anti-inflammatory drug and a non-sterane arylcarboxylic acid containing only one phenyl group) was examined. The impact of the hydroperoxyl radical/superoxide radical anion pair using two different radical scavengers,  $HCOOH$  and  $HCOONa$  was also examined. The results show that the dissolved oxygen reduced the transformation rate of ibuprofen, because of the model compound competes with the oxygen molecule for  $\cdot H$ . Moreover, this study points out that the ibuprofen reacts with  $O_2^{\cdot -}$  more effectively than with  $HO_2^{\cdot}$ .

### INTRODUCTION

Nowadays, increasing amounts of chemicals such as pesticides, pharmaceutical products are being produced. Some of these compounds are stable and non biodegradable, thus they can pollute our environment. Consequently, efficient technologies are needed to remove them from wastewaters and drinking water.

Ibuprofen ((*RS*)-2-(4-(2-methylpropyl)phenyl)propanoic acid) (*Fig. 1*) is a pharmaceutical with analgesic, anti-pyretic and anti-inflammatory properties. With an annual production of several kilotonnes, thus it is the most widely used member of a diverse class of pharmaceuticals termed non-steroidal anti-inflammatory drugs (NSAIDs). Environmental concentrations of ibuprofen have been found to range from ppt to ppb levels ([Buser et al., 1999](#), Santos et al., 2010).



**Fig. 1:** The chemical structure of ibuprofen

During this work we used photolysis with high energy vacuum ultraviolet (VUV) photons for transformation of ibuprofen. For practical purposes, the use of Xe excimer lamps is the most preferred, because the energy of the radiation ( $\lambda_{\text{max}}=172\text{ nm}$ ) is enough for the homolytic dissociation of water molecules, thus it initiates radical reactions.



These primary radicals form in a small volume surrounded by water molecules (solvent cage) and therefore their recombination is highly favoured.

Although there is plenty of information available about the reactions of the most reactive radical, the hydroxyl radical ( $\cdot\text{OH}$ ), only a few data is given concerning the less reactive radicals (e.g. hydroperoxyl radical/superoxide radical anion ( $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ )), which might also contribute to the degradation of the pollutant molecules. Using radical transfers in great excess the degradation of the target compounds may be initiated by radicals, which formed in the reactions between the transfer molecules and the primary radicals.

In this research the effect of dissolved oxygen and the formate ion (in formic acid and dissociate salt form) were investigated on the VUV photolytic degradation of ibuprofen.

## MATERIALS and METHODS

### Reactor configurations

Our measurements were performed in the apparatus containing a 20 W xenon excimer lamp (Radium Xeradex<sup>TM</sup>, at the center of the reactor) emitting at  $172\pm 14\text{ nm}$  of wavelength. 250 ml solutions were circulated by a peristaltic pump between the reactor and reservoir tanks (both thermostated at  $25 \pm 0.5\text{ }^\circ\text{C}$ ) at  $375\text{ ml min}^{-1}$  flow rate. To investigate the factor of oxygen,  $\text{O}_2$  gas (99.995 % purity) or  $\text{N}_2$  gas (99.995% purity) was bubbled through the solutions starting 15 or 30 minutes before and until the end of the irradiation. The  $c_0$  values of ibuprofen,  $\text{HCOOH}$  and  $\text{HCOONa}$  were  $1.0\times 10^{-5}\text{ mol L}^{-1}$ , 0.50 and  $0.05\text{ mol L}^{-1}$ , respectively.

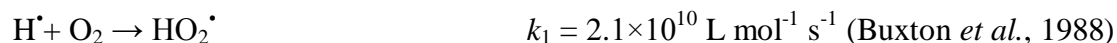
### Analytical methods

The samples (20  $\mu\text{l}$ ) were analyzed using an Agilent 1100 HPLC equipment (LiChroCART® C18 reverse-phase column) with a diode array detector. In our case acetonitrile and 1% aqueous acetic acid were used in 1:1 ratio as eluent, at a flow rate of  $0.8\text{ ml min}^{-1}$ . The quantification wavelengths for the UV detector were 220 and 260 nm in the case of ibuprofen containing solutions.

## RESULTS

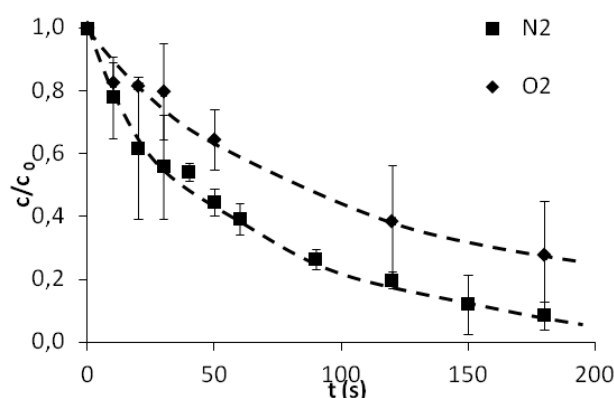
### The effects of dissolved $\text{O}_2$

A widely used radical transfer is dissolved  $\text{O}_2$ , which hinders the recombination reaction of  $\text{H}\cdot$  and  $\cdot\text{OH}$ , thus increases the concentration of  $\cdot\text{OH}$  and converts reductive  $\text{H}\cdot$  to oxidative  $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ .



There is no significant difference between the values of the reaction rate constants of ibuprofen with primary radicals, such as  $\text{H}\cdot$  and  $\cdot\text{OH}$  ( $4.0\times 10^9\text{ L mol}^{-1}\text{ s}^{-1}$  (Illés *et al.*, 2013),  $6.1\times 10^9\text{ L mol}^{-1}\text{ s}^{-1}$  (Jones *et al.*, 2007)), thus  $\text{O}_2$  might compete with ibuprofen for the  $\text{H}\cdot$ . Regarding to the concentration of ibuprofen and dissolved molecular oxygen, we can suppose that in solutions saturated with oxygen the  $\cdot\text{H}$  reacts mainly with oxygen and its reaction with ibuprofen strongly suppressed.

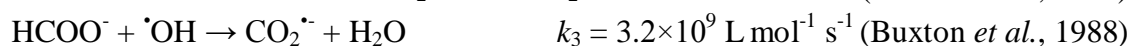
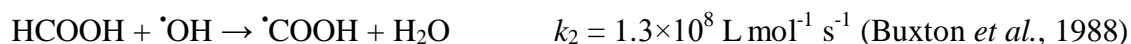
On the other hand, the  $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$  radicals that are generated in presence of oxygen do not contribute to the transformation of ibuprofen significantly. Consequently, even though the concentration of  $^\bullet\text{OH}$  increases in the presence of  $\text{O}_2$ , the rate of transformation of ibuprofen decreases (Fig. 2) most likely because of the strong decrease of the concentration of  $\text{H}^\bullet$ .



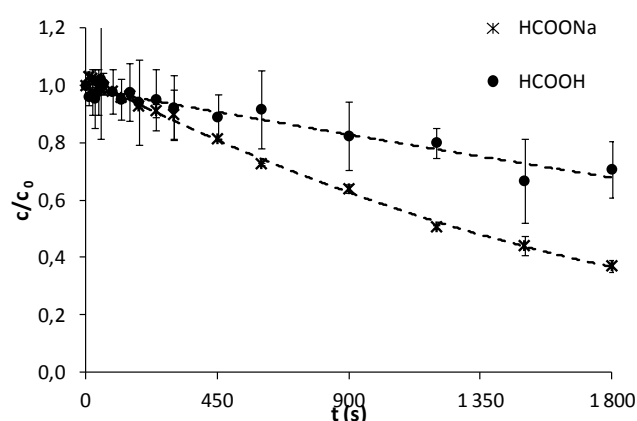
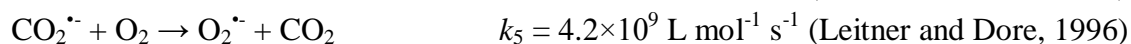
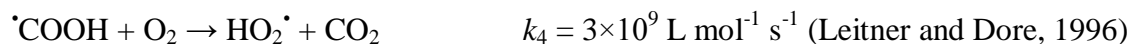
**Fig. 2:** Kinetic curves of ibuprofen ( $c_0=1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in the absence and in the presence of dissolved oxygen during vacuum ultraviolet photolysis

### The effects of formate ions

Another known radical transfer material is the formate (in  $\text{HCOOH}$  or  $\text{HCOO}^-$  form) because it reacts with  $^\bullet\text{OH}$  and results in formyl radical/carbon dioxide radical anion ( $^\bullet\text{COOH}/\text{CO}_2^{\bullet-}$ ) having negligible reactivity towards organic substances.



In the presence of  $\text{O}_2$ ,  $^\bullet\text{COOH}/\text{CO}_2^{\bullet-}$  transform to  $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ .



**Fig. 3:** The effect of addition of  $\text{HCOOH}$  ( $0.50 \text{ mol L}^{-1}$ ) and  $\text{HCOONa}$  ( $0.05 \text{ mol L}^{-1}$ ) on the kinetic curves of ibuprofen ( $c_0 = 1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in oxygen saturated solutions during vacuum ultraviolet photolysis

In oxygen saturated and formate ion containing solutions all primary radicals can be transformed to  $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ . Consequently, the rate of transformation of ibuprofen significantly decreased. In the case of addition of  $\text{HCOOH}$  at  $\text{pH} \sim 3.9$ , 90% of the radicals appear in  $\text{HO}_2^\bullet$ .



form, while using HCOONa, at pH~10.5, the radicals are almost completely transformed to  $O_2^{\cdot-}$ . As Fig. 3 shows, the rate of transformation was found to be higher using HCOOH than HCOONa. Most likely explanation of this experimental fact is that, ibuprofen reacts with  $O_2^{\cdot-}$  more effectively than with  $HO_2^{\cdot}$ .

## CONCLUSIONS

- In the present study we investigated the effect of dissolved molecular oxygen and formate ion during vacuum ultraviolet photolysis of ibuprofen.
- The dissolved molecular  $O_2$  reduced the transformation rate of ibuprofen in a low concentration ( $1.0 \times 10^{-5}$  mol L<sup>-1</sup>), most likely because of the decrease of the  $H^{\cdot}$  concentration overcompensates the effect of the increase of  $^{\cdot}OH$  concentration.
- Using formate ion as radical transformer, all primary radicals can be transformed to  $HO_2^{\cdot}/O_2^{\cdot-}$  in oxygen saturated solutions.
- Ibuprofen might react with  $O_2^{\cdot-}$  more effectively than with  $HO_2^{\cdot}$ .

## ACKNOWLEDGEMENT

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# THE EFFECT OF RADICAL TRANSFER MATERIALS (O<sub>2</sub>, HCOOH, HCOONa) ON THE VACUUM ULTRAVIOLET PHOTOLYSIS OF IBUPROFEN

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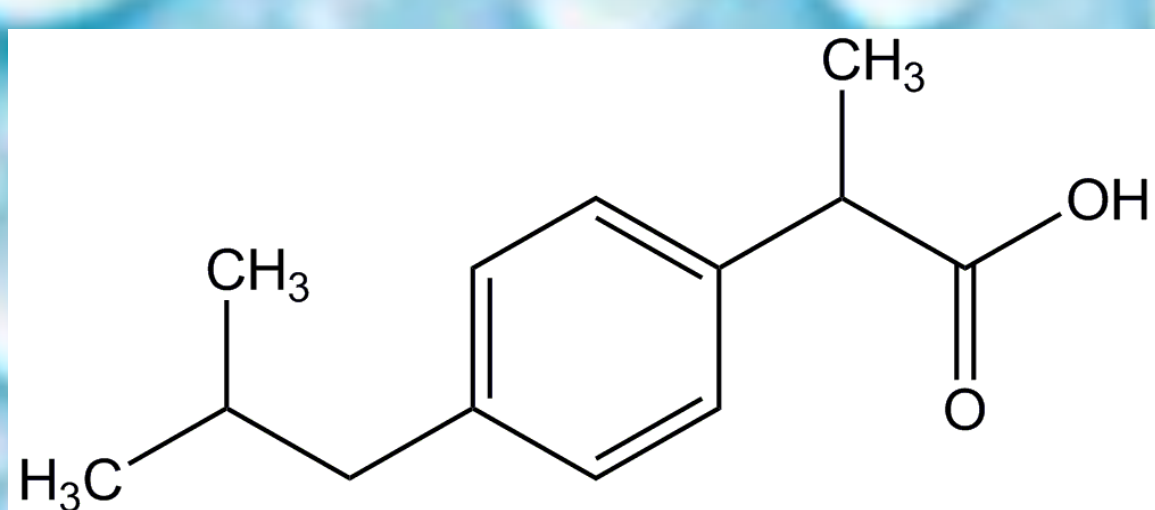
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## ABSTRACT

Nowadays, one of the emerging additive technologies for treatment of water are advanced oxidation processes (AOPs), which are based on the generation of reactive free radicals to induce the transformation of the organic contaminants. Vacuum ultraviolet (VUV) photolysis is a clear and easy method for the generation of reactive radicals (hydroxyl (•OH) and hydrogen (H•) radicals) without the addition of chemicals, using Xe excimer lamp ( $\lambda_{\text{max}}=172$  nm). During this work the VUV photolytic degradation of ibuprofen (a non-steroidal anti-inflammatory drug and a non-sterane arylcarboxylic acid containing only one phenyl group) was examined.. The impact of the hydroperoxyl radical/superoxide radical anion pair using two different radical scavengers, HCOOH and HCOONa was also examined. The results show that the dissolved oxygen reduced the transformation rate of ibuprofen, because of the model compound competes with the oxygen molecule for •H. Moreover, this study points out that the ibuprofen reacts with O<sub>2</sub><sup>•-</sup> more effectively than with HO<sub>2</sub><sup>•</sup>.

## EXPERIMENTAL

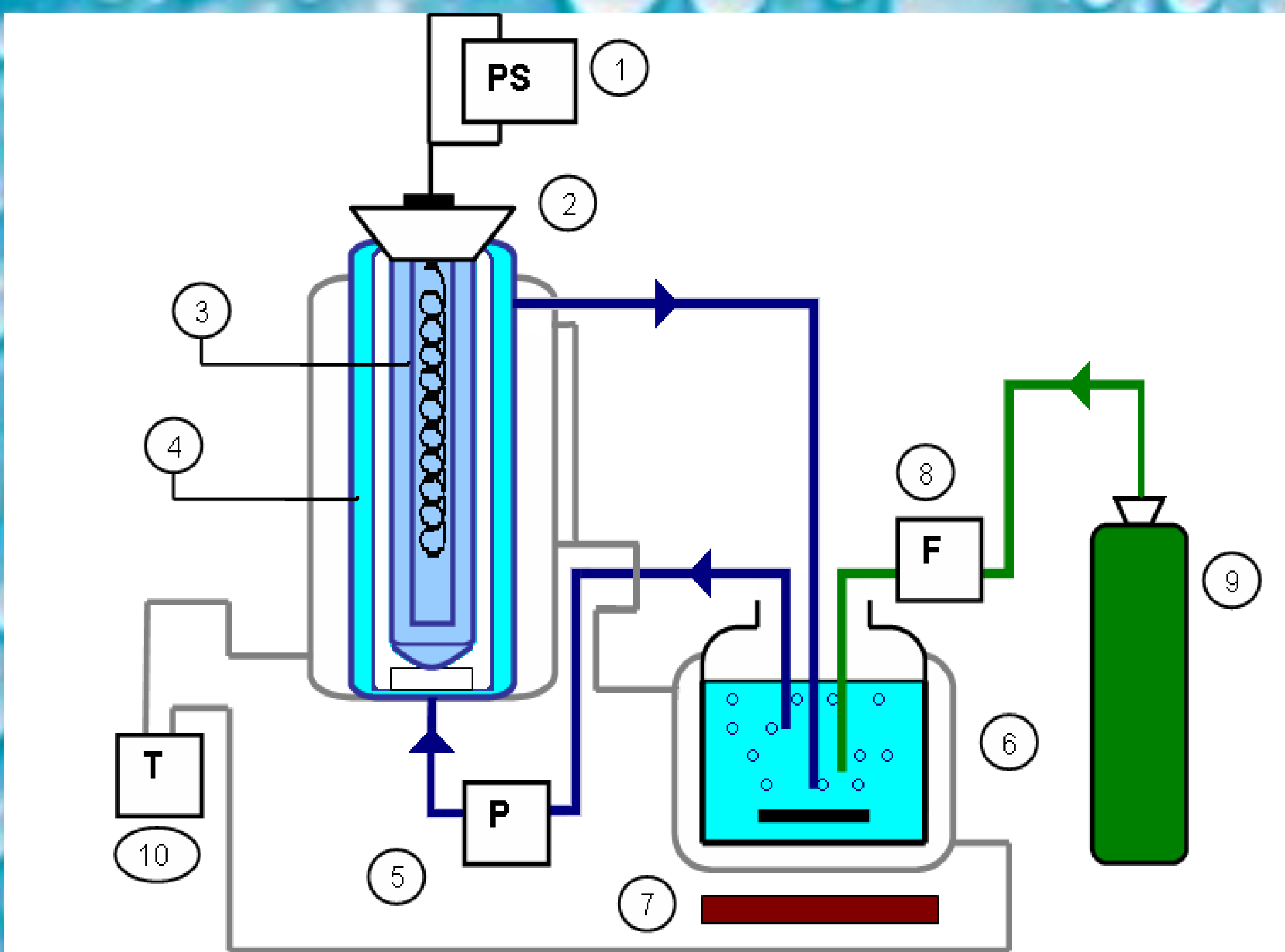


The chemical structure of ibuprofen

1.0×10<sup>-5</sup> mol L<sup>-1</sup> ibuprofen solutions were irradiated by Xe excimer lamp. The experiments gas through the solutions were carried out by bubbling oxygen or nitrogen to investigate the effect of dissolved molecular oxygen.

The experiments were performed in the apparatus depicted below, containing a **20 W** xenon excimer lamp (Radium Xeradex™) emitting at **172±14 nm** of wavelength. The lamp was placed at the center of the thermostated reactor tube isolated from the liquid phase by a cover made of Suprasil® quartz. A peristaltic pump circulated the treated solutions of **250 cm<sup>3</sup>** between the reactor and reservoir tanks (both thermostated at **25±0,5 °C**) at **375 cm<sup>3</sup> min<sup>-1</sup>** flow speed. To achieve oxygen-saturated conditions, **oxygen gas** (99.995 % purity) was bubbled through the solutions starting **15 minutes** before and until the end of the irradiation. For deoxygenized conditions, **nitrogen gas** (99.995% purity) was inducted into the solutions starting **30 minutes** before the irradiation. The change in pH during the experiments was also monitored using an inoLab pH 730p instrument.

The samples were analyzed using an Agilent 1100 HPLC (LiChroCART® C18 RP column) equipped with a diode array detector. Acetonitrile and 1% aqueous acetic acid were used in 1:1 ratio as eluent, at a flow rate of 0,8 cm<sup>3</sup> min<sup>-1</sup>. The quantification wavelengths for the UV detector were **220** and **260 nm** in the case of ibuprofen containing solutions.

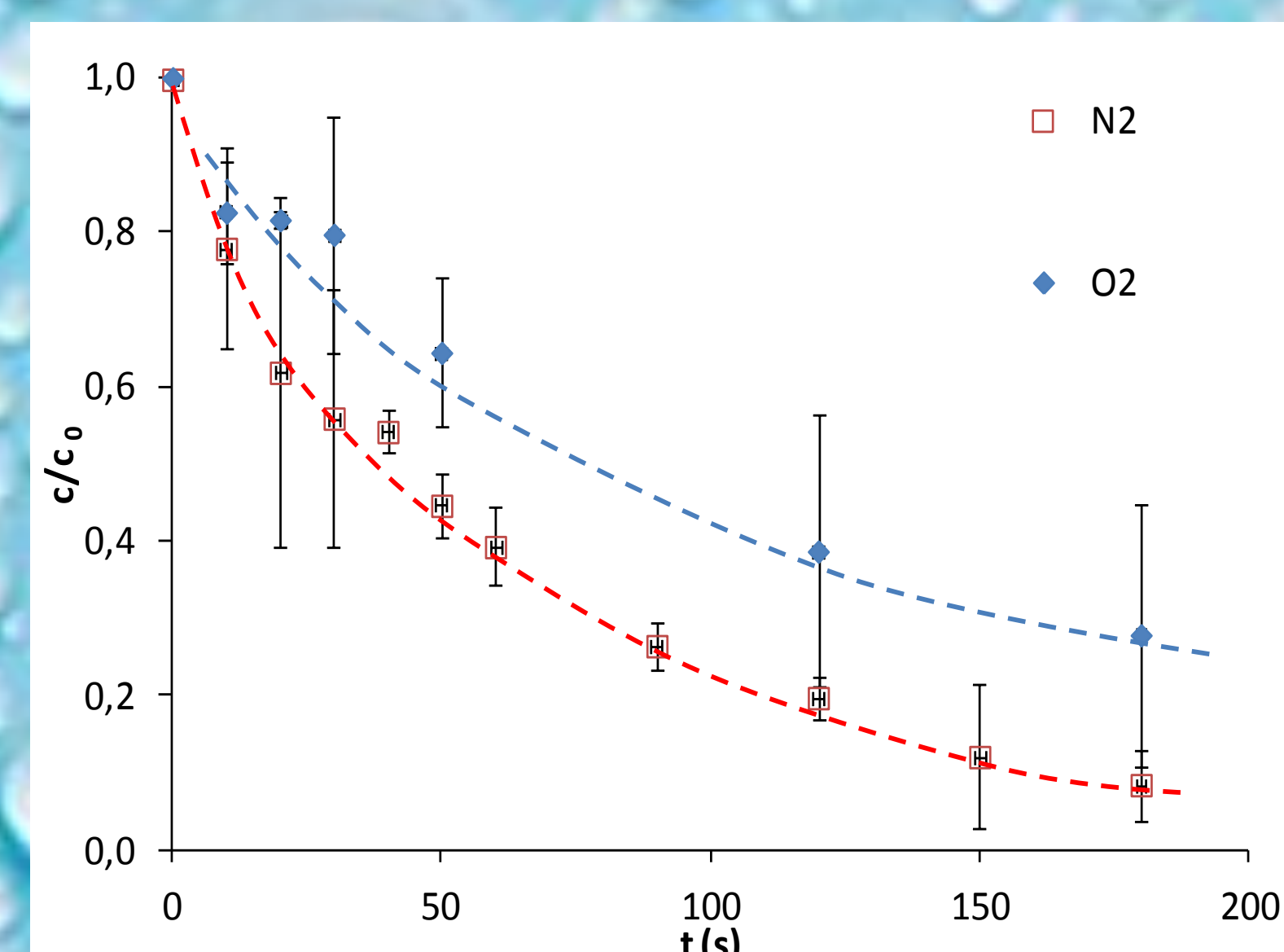


### Photochemical apparatus:

**1:** power supply; **2:** teflon packing ring; **3:** xenon excimer lamp; **4:** reactor; **5:** peristaltic pump; **6:** reservoir; **7:** magnetic stirrer; **8:** flow meter; **9:** O<sub>2</sub> or N<sub>2</sub> bottle and **10:** thermostat

## RESULTS

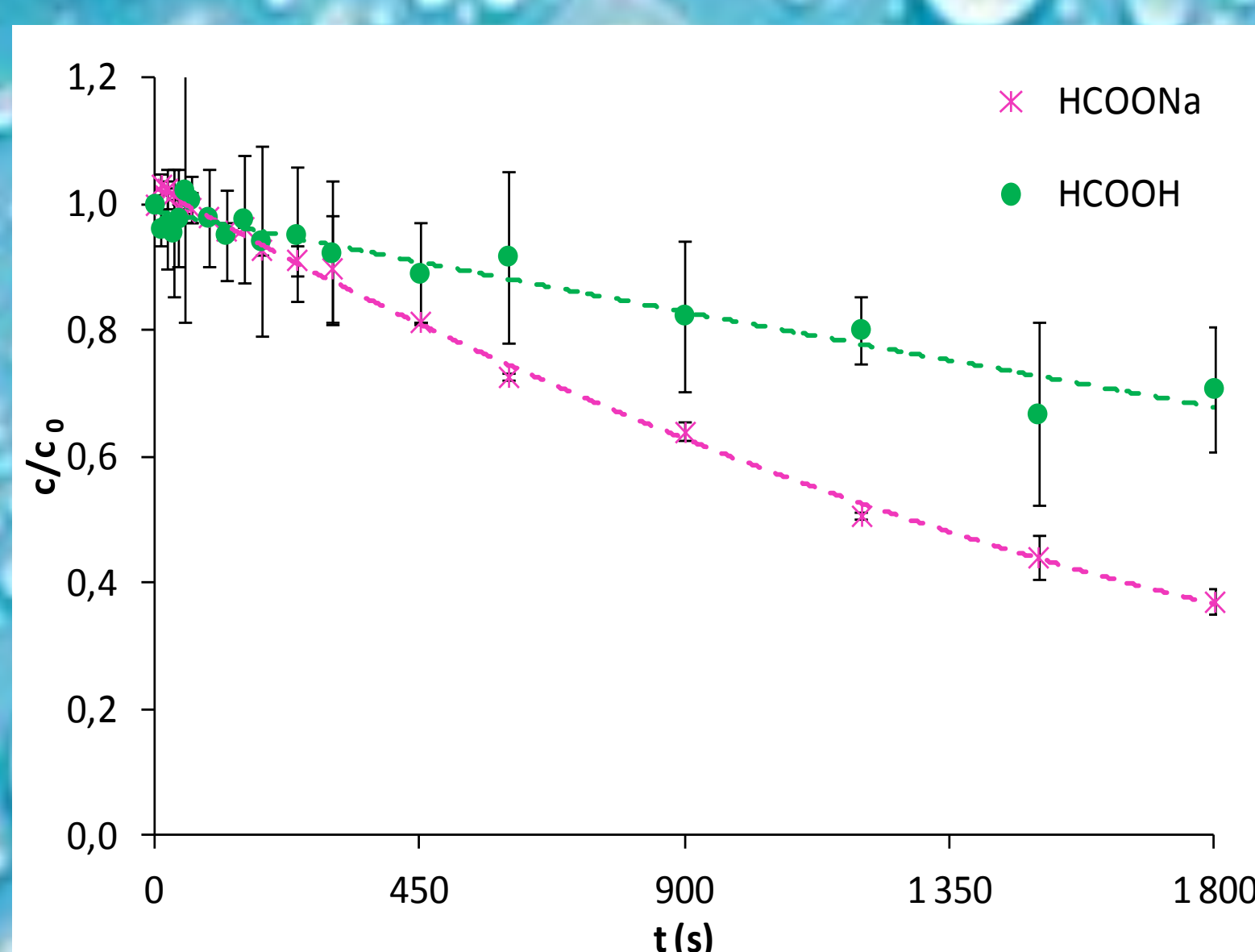
*Kinetic curves of ibuprofen in absence and in presence of dissolved oxygen during VUV photolysis*



### The effects of dissolved O<sub>2</sub>

A widely used radical transfer is dissolved O<sub>2</sub>, which hinders the recombination reaction of H• and •OH, thus increases the concentration of •OH and converts reductive H• to oxidative HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>.

The figure shows that the ibuprofen's rate of transformation decreased in oxygen saturated conditions compared to the oxygen free conditions. The ibuprofen reacts with the •H and with •OH at a comparable rate, which can serve as an explanation to the previous observation. The HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup> radicals that are generated in presence of oxygen do not contribute to the transformation of ibuprofen significantly.



The effect of HCOOH and HCOONa on the kinetic curves of ibuprofen in oxygen saturated solutions during VUV photolysis

In formate ion containing solutions all primary radicals can be transformed to HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>. Consequently the rate of transformation of ibuprofen significantly decreased. In the case of addition of HCOOH (pH ~ 3.9), 90% of the radicals appear in HO<sub>2</sub><sup>•</sup> form, while using HCOONa, (pH ~ 10.5), the radicals are almost completely transformed to O<sub>2</sub><sup>•-</sup>. The rate of transformation was found to be higher using HCOOH (0.5 mol dm<sup>-3</sup>) than HCOONa (0.05 mol dm<sup>-3</sup>). Most likely explanation of this experimental fact is that, ibuprofen reacts with O<sub>2</sub><sup>•-</sup> more effectively than with HO<sub>2</sub><sup>•</sup>.

## CONCLUSIONS

- The dissolved molecular O<sub>2</sub> reduced the transformation rate of ibuprofen
- Using formate ion as radical transformer, all primary radicals can be transformed to HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup> in oxygen saturated solutions.
- Ibuprofen might react with O<sub>2</sub><sup>•-</sup> more effectively than with HO<sub>2</sub><sup>•</sup>.